METHODOLOGY

Whole-rock X-ray fluorescence analysis of major and trace elements of 12 samples was carried out at the Geological Survey of Norway using a PANalytical Axios at 4 kW. The precision ($1\sigma$) is typically around 2 rel%.

The major element composition of the phyllosilicates within spherules of six samples was determined at the Museum für Naturkunde (MfN) in Berlin using a JEOL JXA 8500A electron microprobe with a field emission cathode and five wavelength-dispersive spectrometers. Measurements were made at 15 kV acceleration voltage and 30 nA beam current. The sample spot size (surface) was approximately 1 µm. Back-scattered electron images and element mappings were also done with a JEOL JSM-6610LV scanning electron microscope equipped with a Bruker AXS Quantax 800 EDX system at MfN.

Iridium, Ru, Pt, Rh, Pd, and Au abundances were measured in Cardiff by inductively coupled plasma mass spectrometry after being concentrated from 15 g powders by NiS fire assay (see Huber et al., 2001 and McDonald and Viljoen, 2006 for details on the method). Eight samples containing spherules were analyzed and eight samples of basalt, diabase, and pepperite from other depths in the same drill core were measured for background values (see Table 1). In addition, PGEs from two samples of Vredefort granophyre were measured for comparison. The samples BG-9, a spherulitic granophyre, and BG-168, a granular granophyre, were previously used in the study of Koeberl et al. (1996).

REFERENCES


FIGURES

Figure DR1. Simplified geological and geographical map of the Lake Onega region in the Fennoscandian Shield (modified after Koistinen et al. 2001), showing locations of drill cores 12A and 13A.

Figure DR2. Lithostratigraphy, organic matter $\delta^{13}$C profiles, and Ir abundances for the upper parts of cores 12A and 13A, with the positions of spherule-rich beds indicated as stars. Correlation between the cores is based on lithology (Crne et al., 2013a,b) and corroborated by the stratigraphic trends of $\delta^{13}$C of organic matter ($\delta^{13}$C data within core 12A are from Kump et al., 2011; $\delta^{13}$C data for core 13A from L. Kump, accessed via the internal FAR-DEEP website, far-deep.icdp-online.org). The Ir anomaly of the upper and lower spherule-rich layers in core 13A is indicated; no samples were analyzed between the two spherule-rich layers. Lithologies are meta-lithologies.

Figure DR3. A) Backscatter electron scanning electron microscope image of a spherule from core 13A at 27.0 m depth with distinct inner and outer phyllosilicate layers; the density of the phyllosilicates is similar, obscuring the compositional difference. B) Energy dispersive X-ray map of the same spherule, showing a clear separation of core and rim, with the core composed of Si-enriched phyllosilicates. Similar compositions of phyllosilicates are sometimes found in the matrix. The pattern of a rim and the core of a melt spherule is typical of Karelian spherules. The outermost layer of phyllosilicates, compositionally similar to the core, appears petrographically to be a late overgrowth. The pink and yellow colors on the map are the result of overlap of Al and Si, with the pink area being relatively enriched in Si and yellow relatively enriched in Al.

Figure DR4. Chondrite-normalized (after Rudnick and Gao, 2003) platinum group element (PGE) abundances of the spherule intervals in core 13A and in magmatic rocks (grey fields) (See Table 1). Iridium and Ru abundances are clearly elevated in the spherule-rich layer relative to both the magmatic deposits in the core and relative to upper crustal values. U.Crust = upper crust. Crustal values from Rudnick and Gao (2003).

Figure DR5. Comparison of PGE abundance ratios between elements in spherules and magmatic samples from core samples. Individual samples are not plotted; values are determined from a linear regression of all analyses (see Figure 2 of main text), and error bars represent the 95% confidence interval. A) Ru/Rh vs Ru/Ir for spherules, magmatic samples, and various chondrite
groups. B) Pd/Ir vs Ru/Ir for spherules, magmatic samples, and chondritic groups. The spherules are clearly distinct from the magmatic samples and have an apparent chondritic source of PGEs. Likely due to the low abundances of the PGEs in these samples, the type of chondrite cannot be identified. Data for chondrites from Tagle and Hecht (2006).
Figure DR2

Legend:
- Basalt
- Dolostone
- Breccia
- Dolostone–chert
- Greywacke–siltstone
- Breccia with C_{org}-rich matrix
dolostone–chert
- Mudstone
- Massive C_{org}-rich rock
- Calcareous greywacke–siltstone–mudstone
- Mudstone–marl–limestone
- Location of spherule-rich beds
Figure DR4

Element/CI Chondrite

Ir, Ru, Rh, Pt, Pd, Au

26.90 m, 26.95 m, 26.96 m, 27.28 m, 27.36 m, 67.11 m, 67.12 m

U. Crust, Granophyre
Figure DR5

(a) Chondrites

(b) Magmatic Spherules

Chondrites

Magmatic

Spherules